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Procedia Engineering 93 (2014) 2 – 7

Procedia Engineering

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,MRS Singapore - ICMAT Symposia Proceedings

Carbon Nanotubes and Graphene: Synthesis, Functionalisation and Applications

Density Functional Theory Study of Metal Adatoms At or Near a Stone-Wales Defect in Graphene

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Abstract

Research interest of small clusters of the transition metals continues to grow given their wide range of applications. In recent years, graphene with vacancy and structural defects have attracted increasing attention due to the fact that manufactured graphene is often not pristine, and crystal defects are considered useful in the context of modifying and engineering the band structure of graphene, hence altering both its physical and chemical properties significantly. Previous studies done on the Stone-Wales defect shows that C–C bonds associated with Stone-Wales defects are more reactive than the case for a perfect hexagon. In this work, we investigated the structural, electronic and magnetic properties of Co, Rh and Ir adatoms and dimers in various configurations adsorbed on a graphene sheet with a Stone-Wales transformation. We are interested in the change in bonding and the change in electronic and magnetic properties as a result of the presence of the metal adatom near the Stone-Wales defect by comparison to previous work done where the adatom was adsorbed on graphene with no defects. The results of this work will impact our view on the application of small metal clusters adsorbed on defected or non-defected graphene. Our results show that the Stone-Wales defect significantly increased the adsorption energy by 0.32 eV of a Co atom positioned at the hole site of a 6-carbon ring but the magnetic moment showed no significant change. Hence, the Stone-Wales defect could be used to significantly alter the stability of the adsorption of adatoms on graphene.

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Adatoms, Stone-Wales, Defect, Graphene

Nomenclature

ΔE	Adsorption Energy of (eV)

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Selection and/or peer-review under responsibility of the scientific committee of Symposium [Symposium G - Carbon Nanotubes and Graphene: Synthesis, Functionalisation and Applications] – ICMAT
doi:10.1016/j.proeng.2013.11.021

1. Introduction

Research interest of small clusters (n<5) of the transition metals continues to grow given their wide range of applications from molecular electronics, spintronics, to catalysis. The reason for this is the diversity of structural and electronic behaviors that occur, which are usually nonscalable and rather sensitive to minor changes in the composition of atoms. [1] In recent years, studies have been done, both experimentally and theoretically, in both the gas phase [2], and when these metal clusters are embedded within [3], or adsorbed on a suitable substrate. A variety of substrates have been studied, including metals like Cu [4] and carbon allotropes like graphite. [5]

An ideal substrate is one that is suitably inert in terms of its reactivity with the transition metal clusters, but at the same time, allows for the clusters to bind sufficiently well to it, and hence does not alter the physical and chemical properties of the metal cluster compared to when it is free. Research has shown that while metal surfaces interact rather strongly with metal clusters, graphite is reasonably inert. Since the isolation of graphene in 2004, much work has been done on the unique physics associated with this material. Fundamentally, these properties of graphene are attributed to its massless electrons, which in turn give rise to a host of applications, in particular quantum-based applications that would not be considered at room temperature. [6] Graphene also functions as a support material or substrate. Other materials, which serve various functions themselves from catalysts to magnetic nanoclusters, have been deposited on graphene and investigated both theoretically and experimentally. [7] However, some studies show that adatoms and dimers bind weakly to graphene with binding energies ranging from 0.2 to 1.4 eV for adatoms and 0.1 to 0.5 eV per metal atom for dimers, depending on the adsorption site and species. [8]

In recent years, graphene with vacancy and structural defects have attracted increasing attention. This interest stems from two reasons. First, graphene that is manufactured is often not pristine. [9] Second, crystal defects like the Stone-Wales defect are considered useful in the context of modifying and engineering the band structure of graphene, hence altering both its physical and chemical properties significantly. [10] This, in turn, increases the range of applications of this intriguing material. A Stone-Wales transformation is a dipole of 5–7 ring pair in a hexagonal network, a defective structure seen in carbon allotropes. Previous studies done on the Stone-Wales defect shows it has a significant impact on both the mechanical properties [11] and that C–C bonds associated with Stone-Wales defects are more reactive than the case for a perfect hexagon, thus enhancing the stability of the adsorption of Ni atoms.[12] However, results from previous studies on nitrogen substitutional doping in Stone-Wales defects in zigzag-edged graphene nanoribbons (ZGNRs) and carbon nanotubes suggest that there was no significant effect on the electronic properties for some doping sites [13] and the transport property of the nanotubes was enhanced or weakened depending on their band structure. [14] In this work, we investigate the structural, electronic and magnetic properties of Co, Rh and Ir adatoms and dimers in various configurations adsorbed on a graphene sheet with a Stone-Wales transformation.

2. Research focus

2.1. Hypothesis

In the context of structure (i.e. geometry), we are interested in the change in bonding as a result of the presence of the metal adatom near the Stone-Wales defect. The change in the electronic and magnetic properties of both the metal adatom and the graphene is also investigated and compared to previous work done where the adatom was adsorbed on graphene with no defects. The results of this work will impact our view on the application of small metal clusters adsorbed on defected or non-defected graphene. At the same time, fundamental understanding of the nature of the Stone-Wales defect and its importance in physical and/or chemical processes will also be alluded to.

Our hypothesis is that both the electrical and magnetic properties of the metal adatom and graphene with a Stone-Wales defect will be more significant than graphene with no defects because we hypothesize that the carbon atoms at or near a Stone-Wales defect are more reactive. Also, when placed above a carbon atom in graphene with a Stone-Wales defect, the Co, Rh and Ir adatoms will be able to have sufficient affinity with the carbon atom to form a diverging pattern and results in greater curvature of the underlying graphene.

2.2.Research Method and Materials

In this project, the plane-wave based density functional theory program PWscf (ESPRESSO Version 3.2) was used to perform all calculations. [15] The Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) ultrasoft pseudopotential with nonlinear core correction [16] was used for all species (Co, Rh, Ir) with the Perdew-Burke-Ernzehof (PBE) generalized gradient approximation (CGA) correction [17] formalism employed for the exchange-correlation functional. All pseudopotentials were obtained from the PWSCF pseudopotential online reference. Smearing was used to aid self-consistent-field convergence. Specifically, the Marzari-Vanderbilt method [18] or cold smearing with a small Gaussian spread of 0.01 Ry or 0.13 eV was used. A (4x4x1) Monkhorst-Pack grid was used in the calculations.

3. Interpretation of Data, Results and Findings

In this project, there were 3 types of configurations were investigated, which are summarized in Figure 1. Configuration 1.n.0 consists of a metal atom, Co, Rh or Ir, adsorbed above the hole site formed by n number of carbon atoms, configuration 1.a0b.1 refers to a metal atom adsorbed on the bridge site, which is the mid-point of a carbon-carbon bond, formed by carbon rings with a and b number of carbon atoms, and configuration 1.def.1 refers to a metal atom adsorbed above a carbon atom where d, e, and f are the number of carbon atoms in the adjacent carbon rings.

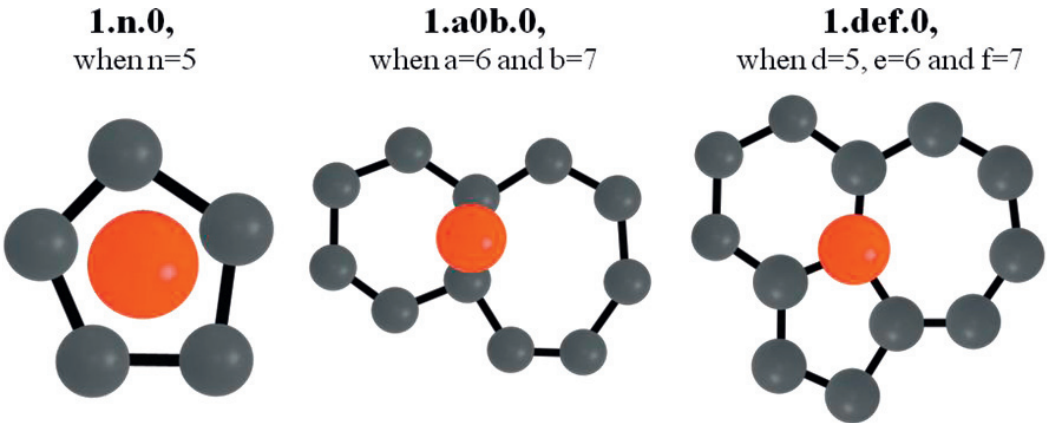

Figure 1. Illustration of the adatom configurations investigated (top view), where the adatoms are Co, Rh or Ir. The pentagon, hexagon and heptagon are formed by carbon atoms in the graphene sheet at or near the Stone-Wales defect.

At the start of the calculations, the metal adatoms were positioned in various configurations, namely 1.5.0, 1.6.0, 1.7.0, 1.566.1, 1.567.1, 1.577.1, 1.666.1 and 1.667.1. As seen from the final configurations listed in Table 1, it was noted that for all the runs, the metal adatoms did not remain at, nor migrate to above carbon atom, at the atom site. This means that the atom site is relatively unstable, which may be due to the fact that the metal adatoms achieve more stability at a shorter distance away from the graphene sheet while binding to more carbon atoms.

From Table 1, it appears that the adsorption energies of Co adsorbed at or near a Stone Wales defect is the lowest (1.66 eV) at position 1.5.0, and hence Co.1.5.0 is the most stable configuration for a Co adatom. With adsorption energies -1.89 eV and -1.87 eV, the configurations Rh.1.5.0 and Ir.1.707.1 are the most stable positions for the metal adatoms Rh and Ir respectively. Also, we can conclude that in terms of stability, Rh adatoms bonded to the graphene are more stable than Ir adatoms, which are, in turn, more stable than Co adatoms bonded to graphene with Stone-Wales defect.

It is also noted that while the systems with Co as the metal adatom have a consistent magnetic moment of 1.00 μB, the magnetic moments of the other configurations mainly range from 1.00 μB to 1.04 μB. There are special cases for the configuration of Rh.1.7.0 and Ir.1.7.0, which have magnetic moments of 1.04 μB, higher than the original value of 1.00 μB.

Table 1. Adsorption energy (ΔE), difference between the adsorption energy and the lowest adsorption energy of the listed configurations (E^{max} - ΔE) and the local magnetic moments (*M*) of the configurations of metal adatoms (Co, Rh, Ir) on graphene with a Stone-Wales transformation.

System		ΔE (eV)	E^{max} - ΔE	M (μB)
Co	1.5.0	1.66	0.443	1.00
	1.6.0	1.29	0.077	1.00
	1.7.0	1.48	0.264	1.00
Rh	1.5.0	1.89	0.671	0.12
	1.6.0	1.67	0.451	1.00
	1.7.0	1.83	0.614	1.04
	1.707.1	1.84	0.627	1.00
Ir	1.7.0	1.65	0.435	1.04
	1.606.1	1.22	0.000	1.00
	1.607.1	1.78	0.563	1.00
	1.707.1	1.87	0.655	1.00

As seen from Table 2, the adsorption energies of the systems where the Co adatom is at or near a Stone-Wales is significantly higher for the hole sites 1.5.0 and 1.7.0, and there is a marked increase (0.32 eV) in the adsorption energy even when the metal adatom was positioned at the hole site 1.6.0. This shows that the presence of the Stone-Wales defect had a significant impact on the stability of the Co adatom. However, the magnetic moment of the systems remained constant at 1.00 μB, and hence the presence of the Stone-Wales defect did not affect the magnetization of the system. Thus, it is not proven that the Stone-Wales defect was able to alter the magnetic properties of the systems.

Table 2. Comparison of adsorption energy (ΔE) and magnetic moment (*M*) data with previous work done on Co adatom adsorbed at the hole site of pristine graphene.

		ΔE (eV)		Magnetic moment(μB)	
System		[a]	[b]	[a]	[b]
Co	1.5.0	1.66	0.97	1.00	1.00
	1.6.0	1.29		1.00	
	1.7.0	1.48		1.00	

[a]This work: Metal adatom Co adsorbed at or near a Stone-Wales transformation in graphene
[b]Johll, Kang and Tok: Metal adatom Co adsorbed on pristine graphene (Johll, Kang, 2009)

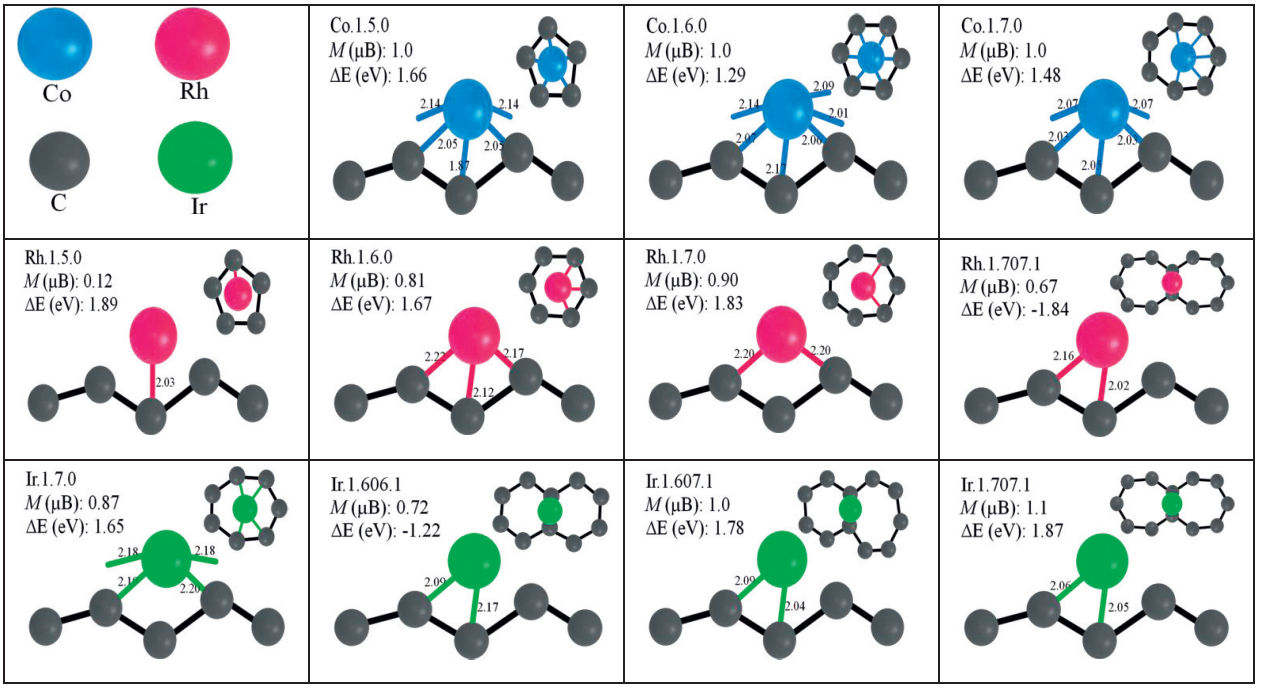

Figure 2. Data for Co, Rh and Ir adatoms adsorbed at or near a Stone-Wales defect in a graphene sheet. The main figure gives the side view i.e., in the *x-z* plane. The side figure gives the top view i.e., the *x-y* plane. The adsorption energies (E_b), the magnetic moments (M), and the bond lengths (Å) are shown. Note that the base atoms represent the graphene sheet.

4. Conclusion and Recommendations

In conclusion, the configurations Co.1.5.0, Rh.1.5.0 and Ir.1.707.1 are the most stable configurations for the respective metal adatoms of Co, Rh and Ir. Out of all the configurations, Rh.1.5.0 has the lowest adsorption energy of 1.89 eV and is hence an Rh atom in the 1.5.0 configuration has achieved the most stable position out of all the investigated configurations.

The data in this work was also compared to previous work done. Hence, although the magnetic moment of the configurations was not significantly impacted by the presence of the Stone-Wales defect, the difference in the adsorption energies showed a marked increase in the stability of the adatom.

Future work could focus on the analysis of the results, for example the electronic configurations in the respective configurations, the charge transfer, as well as the distance between the metal adatom and the graphene plane. For a broader range, more research could also be done on Co, Rh and Ir dimers adsorbed at or near a Stone-Wales defect on graphene, to have a comparison or greater depth with the results presented in this paper.

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